PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Hollow Particles

I, JAMES GEORGE FIFE, M.Sc., Ph.D., F.R.I.C., Consulting Chemist and Chartered Patent Agent, of Bank Chambers, 329, High Holborn, London, W.C.1, a British Subject, do
5 hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, (as communicated to me by The Standard Oil Company, a corporation organised under the
10 laws of the State of Ohio, United States of America, of Midland Building, Cleveland, Ohio, United States of America), to be particularly described in and by the following statement : —
15 The present invention relates to a process of forming hollow particles from film-forming material, and to the particles which are produced by this process.

Hollow particles formed of plastic material
20 have heretofore been prepared for a variety of uses. However, it has been found quite difficult to prepare hollow particles which are completely free from holes. In consequence, such particles, when placed on the surface of
25 a liquid of low viscosity and surface tension, quickly fill with liquid and sink to the bottom.

In accordance with the invention, a solution comprising a volatile solvent having dissolved therein film-forming material and a latent gas
30 is subdivided into droplets and the droplets are then subjected to a drying temperature at which the solvent is volatilized and a hole-free tough surface skin is formed on the particles, and at which the latent gas is converted
35 into a gas. In this way gas is liberated within the particle coincident with its formation and is trapped beneath the surface skin of the particle, and either forms a hollow space therewithin or finds its way into a hollow space other-
40 wise formed therein, and through its presence there tends to prevent collapse of the particle walls under pressure of the atmosphere.

The term "latent gas material" is used herein to refer to any material, whether solid, liquid
45 or gaseous, which can be dissolved in the solvent employed to dissolve the plastic material

and which can be converted into a gas, i.e., which produces a gas or is rendered gaseous, at an elevatetd temperature, preferably a temperature at which the synthetic plastic solution 50 may be dried. The agent may itself be a gas, which prior to the conversion is in dissolved form in the solvent, or it may be a liquid or solid which volatilizes or reacts with another material or substance or decomposes to form 55 a gas at such a temperature.

For example, if water is employed as the solvent, dissolved gases which may be employed include dissolved carbon dioxide, methyl chloride and ammonia, while if an or- 60 ganic solvent is employed, dissolved gases such as methyl chloride, dimethyl ether, ethylene oxide, methyl amine, methyl bromide, and dimethyl amine may be used.

There are a large number of liquid and 65 solid substances which are decomposable at elevated temperatures or react with other materials or substances to produce gases, and are designated by the art as " blowing agents." These substances are widely used to produce 70 cellular plastics and plastic foams. Any blowing agent may be employed in the process of the instant invention, provided it is soluble in the solution of film-forming material.

Satisfactory blowing agents include inor- 75 ganic and organic salts selected from the group consisting of carbonates, nitrites, carbamates, oxalates, formates, benzoates, sulfites and bicarbonates, such as sodium bicarbonate, sodium carbonate, ammonium carbonate, sodium 80 nitrite, ammonium chloride, ammonium carbamate, ammonium bicarbonate, sodium sulfite, calcium oxalate, magnesium oxalate, sodium formate, ammonium benzoate, ammonium nitrite and mixtures forming the same, and or- 85 ganic substances such as p-hydroxy phenylazide, di-N-nitrosopiperazines, polymethylene nitroso-amines, such as di-N-nitrosopentamethylene tetramine (Unicel N.D.) and trimethylenetrinitrosamine and compounds containing two 90 or more groups of the formula CON (alkyl) NO, such as succin-bis (N-nitrosomethylamide);

diazoaminobenzene (the material known under the registered Trade Mark Porofor DB), diazoiso-butyric acid dinitrile (Porofor N), and homologues thereof prepared using cyclo-hexanone (Porofor 254) or methyl ethyl ketone instead of acetone.

Many of the above blowing agents will react with other substances, to instantaneously produce gases. Carbonates and sulfites, for example, such as sodium carbonate and sodium sulfite, react with acids such as hydrochloric or sulfuric to produce carbon dioxide and sulfur dioxide, respectively. Ammonium salts react with bases such as sodium hydroxide to liberate ammonia. Therefore, by feeding in hydrochloric acid solution to a solution of a film-forming material in accordance with the invention containing a carbonate or sulfite just as the solution is entering the atomizer, carbon dioxide or sulfur dioxide is liberated and is present during spray-drying as the gas necessary for forming hole-free hollow particles.

Since the amount of gas or gas-producing substance, collectively termed "latent gas material" herein, that is required will depend upon the weight of the solution and upon the amount of gas formed per unit weight of the latent gas, specific quantities and ranges cannot be given. In general, however, it may be said that an amount in the range of from 0.1% to about 25% by weight of the solution is usually sufficient.

The invention is applicable to the formation of hollow particles from any natural or synthetic film-forming material which is soluble in an acidic, alkaline or neutral aqueous solution, or in an organic solvent, and which can form a solution whose viscosity is sufficiently low to permit subdivision of the solution into small droplets, and which is capable of gelling on evaporation of a solution thereof to form a relatively tough gas-impermeable skin or film.

The term "film-forming material" is used herein to refer to film-forming synthetic plastic materials, as a class, including cellulose derivatives, such as cellulose acetate, cellulose acetate-butyrate, and cellulose acetate-propionate, thermoplastic synthetic resins, such as polyvinyl resins, i.e., polyvinyl alcohol (water- or organic solvent-soluble), polyvinyl chloride, copolymers of vinyl chloride and vinyl acetate, polyvinyl butyral, polystyrene, polyvinylidene chloride, acrylic resins such as polymethyl methacrylate, polyallyl, polyethylene, and polyamide (nylon) resins, and thermo-setting resins in the thermoplastic water- or organic solvent-soluble stage of partial polymerization, the resins being converted after or during formation of the particles into a more or less fully polymerized solvent-insoluble stage, such as alkyd, polysiloxane, phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins. All of these resins are film-forming and therefore capable of forming tough-skinned particles during evaporation of droplets of solutions thereof in aqueous or organic solvents. Natural film-forming materials are also included within the scope of the form, including soybean protein, zein protein, alginates, and cellulose in solution as cellulose xanthate or cuprammonium cellulose. Inorganic film-forming substances such as sodium silicate are also contemplated as within the scope of the above term.

The solvent employed will, of course be dictated by the solubility of the film-forming material used. The solvent should, upon evaporation, be conducive to gelation of the material, so that a tough skin is quickly formed over the surface of the droplet. Water, alcohols, ethers, esters, organic acid, hydrocarbons and chlorinated hydrocarbons, are the most noteworthy satisfactory solvents.

The concentration of the solution of film-forming material is not critical. The lower limit is governed by the size of the particle, for the smallest particles are formed from dilute solutions. The upper limit is set by the viscosity of solutions of the material and by particle size.

It is desirable that the droplets not be so large that shrinkage is great in proportion to the size of the droplet. Shrinkage is also determined in part by the concentration of the solution. It has been found that good results may be obtained with solutions which contain as much as 30% film-forming material, and that optimum results are obtainable with solutions containing from 1% to 15% film-forming material. Solutions as dilute as 0.1% have given satisfactory results. Aqueous solutions which contain from 1% to 10% polyvinyl alcohol (viscosity of a 4% aqueous solution at 20° C. is 4 to 28 cp by the Hoeppler falling-ball method) or from 1% to 30%, preferably 2% to 10%, phenol-formaldehyde resin, are very satisfactory.

The solution is prepared, subdivided into droplets, and dried, by conventional means. The use of spray drying equipment, in which the droplets are dried in a current of hot gas, usually air, is especially advantageous. The drying temperature is adjusted according to the stability and softening point of the film-forming material, the size of the droplets produced and the volatility of the solvent employed. However, because of the cooling effect of evaporation, drying air of very high temperatures may be used without injury to low melting or easily decomposable materials.

The dry particles in accordance with the invention that are produced in conventional spray drying equipment, employing solutions of the concentrations indicated above, are very small. They are ordinarily spherical in shape. Frequently their diameter is about ten times the thickness of the plastic skin surrounding their hollow interior, but these dimensions will depend upon the droplet size produced by the

equipment used and the concentration of the film-forming material in the solution.

The following examples illustrate the invention. Sufficient ammonium hydroxide was added to each solution to make it slightly alkaline, in order to prevent decomposition of the latent gas.

EXAMPLES 1 TO 4

Four aqueous solutions of a water-soluble partially polymerized phenol-formaldehyde resin, (the material known under the Registered Trade Mark Durez 14798) were prepared. One of these solutions did not contain any latent gas, while the other contained, as latent gases, 1% ammonium carbonate, ammonium nitrite, and dinitrosopentamethylenetetramine, respectively.

The solutions were spray dried under the conditions set forth in the table below and the hollow particles obtained were tested in order to determine the number of hole-free particles produced. In this test, hereinafter called the " flotation test," a weighed quantity of the spray-dried particles is floated in a bath of petroleum naphtha and the percentage of the original sample which sinks after 24 hours is determined. In order to pass this test, at least 95% of the sample must float.

The results were as follows:—

Feed Stock Composition	1	2	3	4
Solid	Durez 14798	Durez 14798	Durez 14798	Durez 14798
Wt. %	10	10	10	10
Solvent	Water	Water	Water	Water
Wt. %	90	89	89	89
Latent gas	—	DNPT(1)	$(NH_4)_2CO_3$	NH_4NO_2
Wt. %	—	1.0	1.0	1.0
Operating Conditions				
Air Temp. °F.				
Inlet	700	700	700	700
Outlet	400	400	400	400
Feed rate cc/minute	95	105	111	111
Calcd. recovery wt. %	90	100	91	87

(1) DNPT is dinitrosopentamethylenetetramine

Product Properties	1	2	3	4
Density gms./cc				
Dry bulk	0.412	0.073	0.163	0.091
Liquid displacement	0.944	0.346	0.449	0.353
Gas displacement	1.10	0.551	0.879	0.497
Size (microns)				
Average " subsieve sizer "	14.4	14.6	22.4	17.6
Range, microscopic	2—20	2—30	2—30	2—40
Flotation Test				
% Sunk after 24 hours	100	2.0	3.0	1.0

EXAMPLES 5 TO 7

Aqueous polyvinyl alcohol (PVO) solutions were prepared, two of which solutions contained ammonium carbonate and one of which contained ammonium nitrite. The solutions were spray dried under the conditions set forth in the table, and the recovered particles were subjected to the Flotation Test, with the results listed:—

Feed stock:	5	6	7
Plastic material	PVA	PVA	PVA
Wt. per cent.	4.9	5	5
Solvent	H_2O	H_2O	H_2O
Wt. per cent.	95	94.5	94
Latent gas	$(NH_4)_2CO_3$	$(NH_4)_2CO_3$	NH_4NO_2
Wt. per cent.	0.1	0.5	1.0
Decomposition temp. °C.	58	58	80
Operating conditions:			
Air temp. °F.: Inlet	500	600	600
Outlet	230	270	330
Feed rate, cc/min.	95	80	91
Calcd. recovery, wt. %	—	81	73

Product properties:	5	6	7
Density (g/cc)			
Dry bulk - - - - -	0.058	0.068	0.16
Liquid displacement - - -	0.17	0.192	0.39
Gas displacement - - - -	0.29	0.46	0.51
Size (microns)			
Average " subsieve sizer " - -	17.5	23	15.5
Range (microscopic) - -	5—50	5—50	3—30
Flotation test			
% sunk 24 hours - - - -	trace	2	1

PVA=polyvinyl alcohol resin. Viscosity (centipoises) 4—6 in 4% solution in water at 20° C. by Hoeppler falling ball method.

EXAMPLES 8 AND 9

Aqueous solutions of water-soluble partially polymerized phenol-formaldehyde resins were prepared containing 2½% of a commercial blowing agent containing 40% dinitrosopentamethylenetetramine and 60% filler. These solutions were spray dried in standard apparatus under the conditions set forth in the table below, and the particles thereby produced tested, with the following results:—

	8	9
Feed stock:		
Plastic material - - - - -	*Durez 15281	**Bakelite BR 18372
Wt. per cent. - - - - -	10.0	10.0
Solvent - - - - - -	H₂O	water
Wt. per cent. - - - -	89.0	89.0
Latent gas - - - - -	DNPT	DNPT
Wt. per cent. - - - -	1.0 active	1.0 active
Decomposition temp. of latent gas, ° C. - - -	above 100	above 100
Operating conditions:		
Air temp. ° F.: Inlet - - - -	700	700
Outlet - - -	400	450
Feed rate, cc/min. - - - - -	45	66
Calcd. recovery, wt. % - - - -	—	—
Product properties:		
Density (g/cc)		
Dry bulk - - - - -	0.048	0.047
Liquid displacement - - -	0.280	0.211
Gas displacement - - - -	0.681	0.362
Size (microns)		
Average " subsieve sizer " - -	18.6	24.6
Range (microscopic) - -	2—40	5—60
Flotation test		
% sunk 24 hours - - - - -	3.0	1.0

*Water-soluble partially polymerized phenol-formaldehyde resin.
**The word " Bakelite " is a registered Trade Mark.

EXAMPLE 10

An aqueous 10% solution of sodium silicate was prepared containing 2½% of 40% dinitrosopentamethylenetetramine and 60% filler and the solution spray dried. The air temperature at the inlet was 700° F. and at the outlet 360° F., and the solution was fed in at a rate of 153.8 cc. per minute. The calculated particle recovery was 80.6%. The product had a dry bulk density of 0.236 grams per cc., a liquid displacement of 0.580 and a gas displacement of 0.693 grams per cc. The average particle size was 22.2 microns, as determined by a " Subsieve Sizer," and the range of particle size observed in the microscope from 5 to 40 microns.

Two per cent of the particles sank when the material was subjected to the Flotation Test.

EXAMPLES 11 AND 12

This example illustrates the use of a dissolved gas as the gasifying agent.

Aqueous 5% polyvinyl alcohol (viscosity 4 to 6 cp. in 4% aqueous solution at 20° C. by Hoeppler falling-ball method) solutions were prepared and saturated with carbon dioxide and methyl chloride, respectively. The solutions were then spray dried under conditions set forth in the table below, and the particles recovered tested with the following results:—

Feed Stock:		11	12
Plastic material - - - - -		PVA	PVA
Wt. per cent. - - - - -		5.0	5.0
Solvent - - - - - -		H_2O	H_2O
Wt. per cent. - - - - -		95.0	95.0
Latent gas - - - - -		CO_2	CH_3Cl
Wt. per cent. - - - - -		Sat'd (PH. 4.5)	Sat'd
Operating conditions:			
Air temp. ° F. Inlet - - -		445	440
Outlet - -		265	260
Feed rate, cc/min. - - -		99	102
Calcd. recovery, wt. % - -		74	75
Product properties:			
Density (g/cc.)			
Dry bulk - - - - -		0.15	0.13
Liquid displacement - - -		0.57	0.64
Gas displacement - - -		0.61	0.61
Size (microns)			
Average "subsieve sizer" - -		6.8	4.8
Range (microscopic) - - -	5—25		10—35
Flotation test			
% sunk 24 hours - - - -		1.0	1.5

PVA=polyvinyl alcohol

The action of the latent gas in the process of the invention has not been absolutely established by experimental evidence. The following theory has been proposed as a possible explanation in the light of the evidence available, but the invention is not to be limited thereby.

When a solution of film-forming material which does not contain a latent gas is spray dried, hollow particles may be formed, but such particles almost invariably contain holes. It is thought, by way of explanation, that as the solvent evaporates from the droplets, surface shrinkage and surface thickening occurs in the droplet, and these changes continue until the droplet has decreased considerably in diameter and a thick skin, which has sufficient mechanical strength to resist further shrinkage, is formed around the remaining liquid. Thereafter, solvent is lost by diffusion through the skin and a particle is formed having a hollow interior filled with solvent vapor. After the particle is cooled upon emerging from the drying chamber, the solvent vapor within the particle condenses and the pressure within the particle is reduced to the vapor pressure of the solvent at room temperature. The pressure of the atmosphere outside the particle may then become sufficiently great, in relation to the pressure within the particle, to wholly or partially collapse the particle or push in through weak spots in the skin, producing holes.

When a latent gas is present, it is thought that the droplets of solution as solvent evaporates, shrink with formation of a surface skin, as before. Thereafter, latent gas which is converted into gas within the skin is trapped within the droplet. Although the solvent possibly may diffuse out through the skin, this gas is confined in the space therewithin. This gas, if it exerts a sufficient pressure, assists the particle walls in resisting the pressure of the atmos-

phere, so that collapse of the walls or formation of holes therein cannot occur. Also, since the gas pressure within the particle during drying exerts a force on the walls while they are still plastic, the droplet does not shrink nearly as much as when the gas is absent. In fact, if sufficient gas is present it should be possible to form particles of larger diameter than the droplet, the particle walls being expanded while still plastic during formation of gas therewithin. This theory explains why the material employed must be film-forming since, unless a tough, relatively gas-impermeable skin is formed on the surface of the droplet during drying, gas is not retained within the particle in sufficient quantity to develop the necessary pressure.

The small, hollow, hole-free particles produced in accordance with the invention have a wide variety of uses. They may, for example, be used per se as a fill type insulation material, or as fillers in place of granulated cork and like materials of cellular structure in manufacturing molded articles, linoleum and floor tile, or as aggregate in concrete and plaster. The hollow particles may also be adhered together using various techniques or binders, to produce a solid cellular type material of the nature of plastic foam and expanded plastics, for use as thermal, electrical and sound insulation material, plaster board, gaskets, seals, buoys, flotation equipment, aircraft components, boat hulls and decks, shock insulation, ice buckets, toys, decorative items, furniture, and luggage. Sheets of the adhered hollow particles are very useful as honeycomb core materials, as for example in sandwich structures formed by bonding the honeycomb core between two relatively thin, dense, high strength faces or skins to form structural, decorative or special purpose panels. The face materials may con-

sist of plywood, metal, plastic laminates, or others.

Compressible lubricants can be prepared by blending the hollow particles of an oil-resistant resin, such as polyethylene, with oils and greases. This product can be compressed considerably and placed in shock absorber mountings. Under the pressure of the hollow particles, the grease is then forced into the desired places.

A very important field of use for the hollow particles of the invention is in insulation. Because of their small diameter and compressibility due to their hollow structure, the hollow particles can readily be poured into a location, packed under pressure and sealed, as in fill-type insulation material.

Layers of a wide variety of hollow particles prepared as set forth in the preceding examples, were packed in a Fitch apparatus and the thermal conductivity of the layers were determined, with the following results:—

Material	Bulk density g/cc.	Liquid displacement density g/cc.	Particle size average	range	BTU/hr./ ft²/°F. in.
Polyvinyl alcohol	0.012	0.057	38.6	2—110	0.32
Polyvinyl alcohol	0.068	0.192	23.0	5—50	0.31
Phenolformaldehyde	0.080	0.253	24.0	10—70	0.31
Phenolformaldehyde	0.069	0.536	5.6	2—30	0.36
Phenolformaldehyde	0.070	0.346	13.6	2—15	0.30
Protein	0.063	0.80	2.0	2—30	0.32
Polystyrene	0.066	0.173	35.0	2—50	0.34
Methyl cellulose	0.055	0.147	36.5	5—100	0.32
Sodium silicate	0.236	0.552	25.0	5—100	0.45
Sodium aluminate	0.046	0.224	33.6	10—100	0.34
Wood flour					0.42
Granulated cork					0.32
Ohio perlite					0.40
Polyvinyl alcohol powder					0.66

The results show the hollow particles in accordance with the invention to be at least as efficient in insulating capacity as granulated cork and more efficient than any of the other materials tested.

Hollow particles of phenol-formaldehyde resin were prepared having the following properties:—

Sample No.   12

Loose bulk density
     gm./cc. – – – 0.054
     lbs./ft.³ – – – 3.3

Liquid displacement
     Density g./cc. – – 0.229

Particle size, microns
     Average – – – 26.4
     Range – – – 2—60

These hollow particles were packed to a density of 3.9 lbs. per cubic foot and their thermal conductivity measured using a standard flat hot plate apparatus for use at any desired temperature. Thermal conductivity at two sets of temperatures was determined, with the following results:—

Temp. of hot side, °F. – 54.0   135.1
Temp. of cold side, °F. – −2.6   79.9
Mean Temp. °F. – 25.7   107.5
Thermal conductivity – 0.256 0.259
Density under test, lbs./ft.³ 3.9
Density under test, g./cc. 0.062

The thermal conductivity represents the amount of heat in BTU per hour which will flow through one square foot area when the temperature gradient is one degree F. per inch thickness.

The above values represent the thermal conductivity of this sample if used as a fill-type insulation in a refrigerator. The values show that this sample is a very good thermal insulator at ice temperature as well as higher temperatures.

Use of heat and/or a solvent, with application of pressure, is a valuable expedient for setting the hollow particles in the form of a shaped mass after they have been packed into a somewhat inaccessible location as in fill-type insulation.

If the hollow particles are formed of a thermoplastic material, such as cellulose acetate, ethyl cellulose, polyvinyl chloride, polyamides, polyethylene and the like, they may be adhered together in any desired arrangement by slightly softening their surface at an elevated temperature, with application of moderate pressure insufficient to flatten the particles.

More commonly, however, a binder is employed, using one of several techniques. In one procedure, the hollow particles are dispersed in a solution of a suitable binder, such as cutback asphalt, rubber cement or polystyrene dissolved in an organic solvent, or sodium silicate dissolved in water. The solvent is evaporated from the dispersion, depositing the binder upon the hollow particles and adhering them together to produce a solid

mass. The following example illustrates one method of application of this procedure.

EXAMPLE 13.

Hollow particles prepared from a phenol-formaldehyde resin were mixed with a commercial rubber cement solution to produce a heavy paste. A second material was prepared by mixing hollow particles from the same batch with another preparation of commercial grade of rubber cement which had been cut back by addition of 50% benzene. Each of the pastes was spread in a mold and allowed to dry in air for one day at room temperature. The product was cured in an oven at 85° C. for two days.

The two products were similar in appearance. The surface of each was soft and the material was more resilient than natural cork. The first sample had a density of 0.14 or about 8.7 lbs. per cubic foot, while the sample prepared from the 50% cutback rubber cement had a density of 0.11 or 6.8 lbs. per cubic foot.

A second material was prepared by mixing the phenol-formaldehyde hollow particles with a 40° Bé aqueous sodium silicate solution and evaporating the water at an elevated temperature. The solid product obtained was very hard and strong, similar to concrete in appearance. Its density was 0.35 or 23 lbs. per cubic foot. Products having a lower density can be prepared by cutting back sodium silicate solution with water.

Also, if desired, the hollow particles may be dispersed in an emulsion of a suitable binder, such as aqueous rubber latex or polyvinyl acetate emulsion. This procedure can be illustrated as follows:—

EXAMPLE 14.

A 60% neutral aqueous rubber latex emulsion was cut back to 30% with water and mixed with phenol-formaldehyde hollow particles prepared as set forth in Example 3 to produce a thick fluid mass. This was poured into a mold connected with a vacuum and the excess binder drawn off. The product was allowed to dry overnight in air at room temperature and then was placed in an oven and cured at 85° C. for two hours.

The finished product was quite resilient, strong and light in weight. The outer surface was tough and smooth. The material had the resiliency of a medium hard rubber. Its density was 0.15 or about 9.4 lbs. per cubic foot, approximating low density natural cork.

In the case of certain binders, such as asphalt, which have a relatively low melting point, it is possible to disperse the hollow particles directly in the molten binder.

EXAMPLE 15.

Hollow particles of phenol-formaldehyde resin were mixed with resin powder (a thermo-plastic resinous material derived from rosin) having a softening point of 106° C. (R. and B.) on a 50—50 volume basis. The mix was packed in a mold and placed in an oven, where it was held at 120° C. for four hours. The structure had the strength and texture of sandstone. The density of the product was 0.40 or about 25 lbs. per cubic foot.

A strong rigid structure can be prepared by mixing the hollow particles with a solution of a thermosetting resin in a solvent-soluble thermoplastic state, evaporating the solvent and then heating the mixture to convert the resin to a fully-hardened solvent-insoluble non-thermoplastic state.

EXAMPLE 16.

A 50% solution of a water-soluble partially polymerized phenol-formaldehyde resin was diluted to a 10% solution with water. Hollow particles of the same resin were blended into the solution to produce a fluid paste. This was poured into a mold fitted with a vacuum attachment and the excess solvent drawn off by application of vacuum. The product was placed in an oven and held at 85° C. for two hours to remove the water and then baked at 120° C. for four hours to complete polymerization of the resin binder.

The product was quite strong and rigid. It had a density of about 0.15 or 9.4 lbs. per cubic foot.

Sheets or shaped objects of the hollow particles may be bound together by binders prepared in situ by chemical reaction. Portland cement and gypsum plaster are examples of the chemical reaction type of binder.

EXAMPLES 17 AND 18.

Mixes of one part Portland cement and from 3 to 9 parts of the hollow particles with the addition of a small proportion of sand in a few cases, were prepared in the form of cylinders 4.4 cm. in diameter and 8.8 cm. in height. The hollow particles used were of phenol-formaldehyde resin and of polyvinyl alcohol resin. The hollow particles had the following properties:—

Sample No.	17	18
Material	Phenol-formaldehyde Resin	Polyvinyl Alcohol
Density g./cc.		
Bulk - - - -	0.054	0.044
Liquid displacement -	0.239	0.25
Particle size, microns		
Average - - -	26.4	14.4
Range - - - -	2—60	5—70

The mixes were poured in plastic molds where they were allowed to remain for 7 days to retain maximum moisture and then allowed to cure in air for 21 days. This 28-day curing time is standard procedure for preparing concrete to be used in compressive strength tests. After removal from the molds the ends of the samples were levelled and sanded. During

testing a thin sheet of medium hard rubber was placed at each end of the cylinders to assure a maximum surface contact. The test was performed on a hand operated hydraulic press with a 2000 lb. pressure gauge.

The following results were obtained:—

Hollow Particles	Ratio	Density g./cc.	lbs./ft.³	Compressive Strength psi	Ratio Strength/ Density
Phenol-formaldehyde resin	1:3	0.66	41.2	500	12.2
	1:4	0.58	36.0	445	12.2
	1:4.5	0.56	35.0	420	12.0
	1:5	0.53	33.0	370	11.2
	1:5	0.52	32.4	370	11.4
	1:6	0.49	30.6	262	8.5
	1:9	0.39	24.3	183	7.5
Polyvinyl alcohol	1:6	0.65	41.5	430	10.4
Phenol-formaldehyde resin and sand	1:3:3	1.23	77.0	400	5.2
Perlite	1:3	0.70	44.0	400	9.1
	1:6	0.42	26.0	183	7.0
Vermiculite	1:3	0.80	49.8	400	8.0
	1:5	0.53	32.9	221	6.7

These results show that the hollow particles in accordance with the invention are superior to other lightweight aggregate in concrete when used in the same proportions.

The concrete structures obtained could be sawed or nailed without cracking, and had a very fine-grained structure comparable in character to air-entrained concrete.

Concrete containing 3 to 6% air is used in many parts of the country to reduce the spalling of concrete roads due to freezing and thawing. The hollow particles of the invention do not coalesce as does entrained air and can be added in the proper concentration and mixed for any length of time during transportation to a location.

Phenol-formaldehyde hollow particles	Ratio	Density g/cc.	lbs./ft.³	Compression Strength psi
	1:2	0.585	36.5	212
	1:2	0.580	36.2	208
	1:3	0.473	29.5	135
	1:3	0.470	29.0	141
	1:4	0.370	23.1	106
	1:4	0.362	22.6	112
Polyvinyl alcohol hollow particles	1:3	0.56	35	192
Perlite	1:3	0.40	25	159
	1:3	0.427	26.6	164

The results show that the hollow particles of the invention in lightweight plaster have compressive strength values better than Perlite when used in equivalent proportions.

The material was found to be crack and chip resistant, so that it could be sawed or nailed without cracking. Plaster walls made from these hollow particles have excellent insulating and acoustical properties.

EXAMPLES 20 AND 21.

Samples of rigid type insulation material were prepared by dispersing the hollow particles of phenol-formaldehyde resin rubber

EXAMPLE 19.

Lightweight plaster material was prepared by mixing one part fibrous gypsum plaster with from 2 to 4 parts of phenol-formaldehyde resin hollow particles. These mixes were molded in the form of cylinders 4.4 cm. in diameter and 8.8 cm. in height, being allowed to remain in the molds for 7 days and then allowed to air cure for 21 days. After removal from the molds, the ends of the samples were levelled and sanded and their compressive strength determined in a hand operated hydraulic press with a thin sheet of medium hard rubber at each end of the cylinder to assure maximum surface contact. The following results were obtained:—

cement and phenol-formaldehyde resin solutions. The hollow particles used were prepared as set forth in Example 3 and had the following properties:—

Sample No.	20	21
Loose bulk density gm./cc.	0.054	0.080
lbs./ft.³	3.3	5.0
Liquid displacement Density g./cc.	0.229	.253
Particle size, microns Average	26.4	24.0
Range	20—60	10—70

The solvents were removed by evaporation.

In the case of the phenol-formaldehyde resin solution, the solvent was removed by vacuum filters after which the sample was baked in an oven at 185° F. for one hour and then at 220° F. for three hours to complete polymerization of the phenol-formaldehyde resin. The density and thermal conductivity of the samples were then determined, with the following results:—

Sample No.	Binder	Density lbs./ft.^{3}	Average K* BTU/hr./ ft.^{2}/° F./in.
20	rubber cement	10.0	0.43
21	phenol-formaldehyde	14.0	0.29
21	phenol-formaldehyde	8.1	0.32
Cork composition - - - -		15.0	0.34

*Determined by Fitch's apparatus.

The samples have a very low thermal conductivity, comparable to granulated cork and hollow particles alone.

The hollow particles may also be employed as a filler in hard-surface floor materials, such as linoleum, asphalt tile, rubber tile and cork tile. A satisfactory linoleum composition may be prepared by blending the hollow particles in a mixture of oxidized linseed oil and wood flour, replacing the powdered cork filler ordinarily used. Asphalt tile is prepared from asbestos fiber and mineral pigment with an asphalt binder. This tile has excellent wear properties, but is not as resilient as other types of floor covering; the inclusion of hollow particles in asphalt floor tile tends to increase its resiliency.

In the specification all parts and percentages are by weight, unless otherwise indicated.

What I claim is:—

1. A process of forming hollow particles from film-forming material, which includes subdividing into individual droplets a solution comprising a volatile solvent having dissolved therein film-forming material and a latent gas material, and subjecting the droplets to a drying temperature at which the solvent is volatilized at a rate to form a tough, relatively gas-impervious surface skin coincident with particle formation, and the latent gas material is converted into a gas, whereby gas liberated within said forming particle is trapped by the surface skin within the space thereof and through its presence tends to prevent collapse of the particle walls under the pressure of the atmosphere during volatilization of the solvent in order to form particles having a continuous hole-free skin surface.

2. A process in accordance with claim 1 in which the latent gas material is a dissolved gas.

3. A process in accordance with claim 1 in which the latent gas material is a substance which is decomposed at drying temperatures with formation of a gas.

4. A process in accordance with claim 3 in which the substance is dinitrosopentamethylene tetramine.

5. A process in accordance with claim 3 in which the substance is ammonium nitrite or mixture forming the same.

6. A process in accordance with claim 3 in which the substance is ammonium carbonate.

7. A process in accordance with claim 3 in which the substance is ammonium bicarbonate.

8. A process in accordance with claim 1 in which the film-forming material is polyvinyl alcohol.

9. A process in accordance with claim 1 in which the film-forming material is a phenol-formaldehyde resin.

10. Small, discrete, hollow particles of film-forming plastic substantially free of holes and having a gas sealed in the hollow space therein.

11. A shaped mass comprising hollow particles in accordance with claim 10 whose surfaces are bound together.

12. A shaped mass comprising hollow particles in accordance with claim 10 whose surfaces are bound together by adhesion directly to one another.

13. A shaped mass in accordance with claim 11 in which the particles are bound together by a cementitious material.

14. A mass in accordance with claim 13 in which the cementitious material is rigid.

15. A shaped mass in accordance with claim 13 in which the cementitious material is non-rigid.

16. A shaped mass comprising hollow particles in accordance with claim 10 dispersed as a discontinuous phase in a binder as a continuous phase.

17. A shaped mass in accordance with claim 16 in which the binder is concrete.

18. A shaped mass in accordance with claim 16 in which the binder is gypsum plaster.

19. A shaped mass in accordance with claim 16 in which the binder is a synthetic resin.

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